SAENA Workshop 2016

After-treatment systems for diesel engines

Modelling of Aftertreatment Devices for NOx Emissions Control in Diesel Engines

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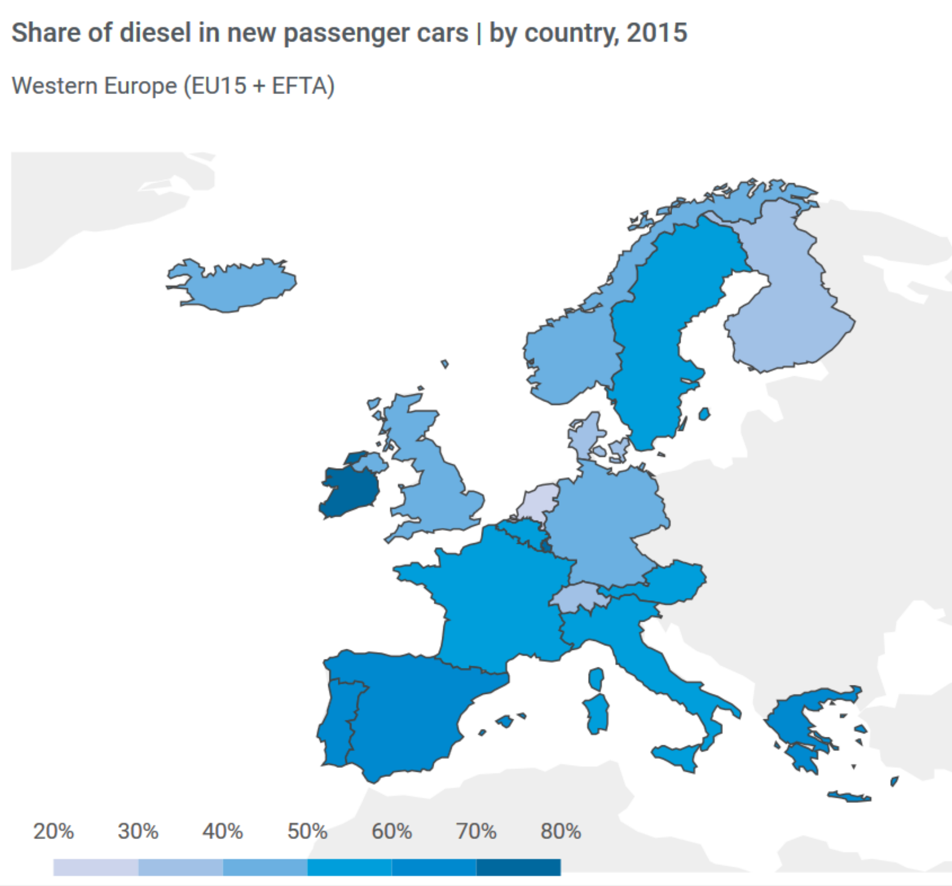
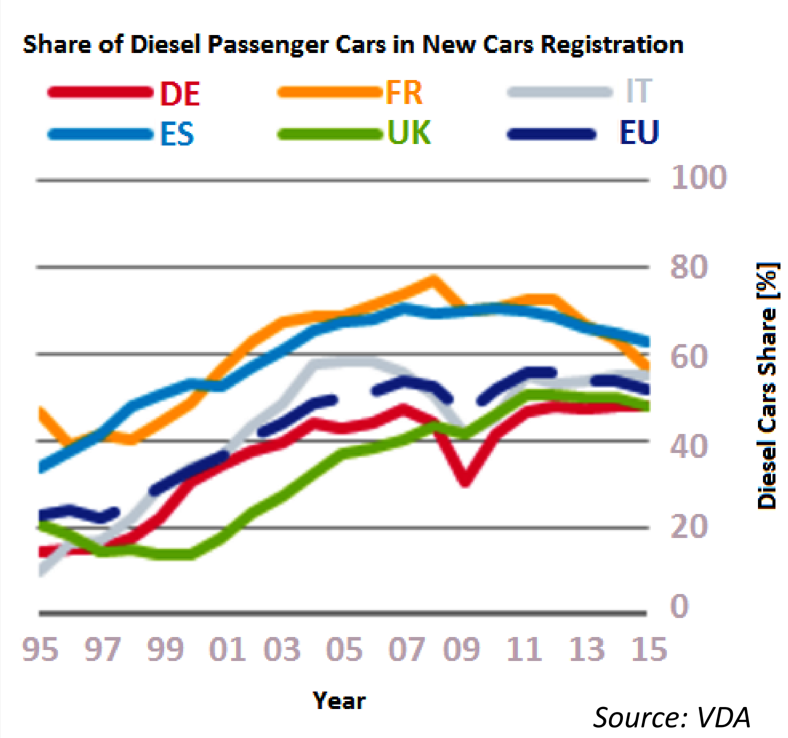
Agenda

- Introduction
- Modelling examples: SCR Coated on Filter
- Modelling examples: Lean NO_x Trap
- Conclusions

Introduction: Diesel Passenger Cars Market in EU

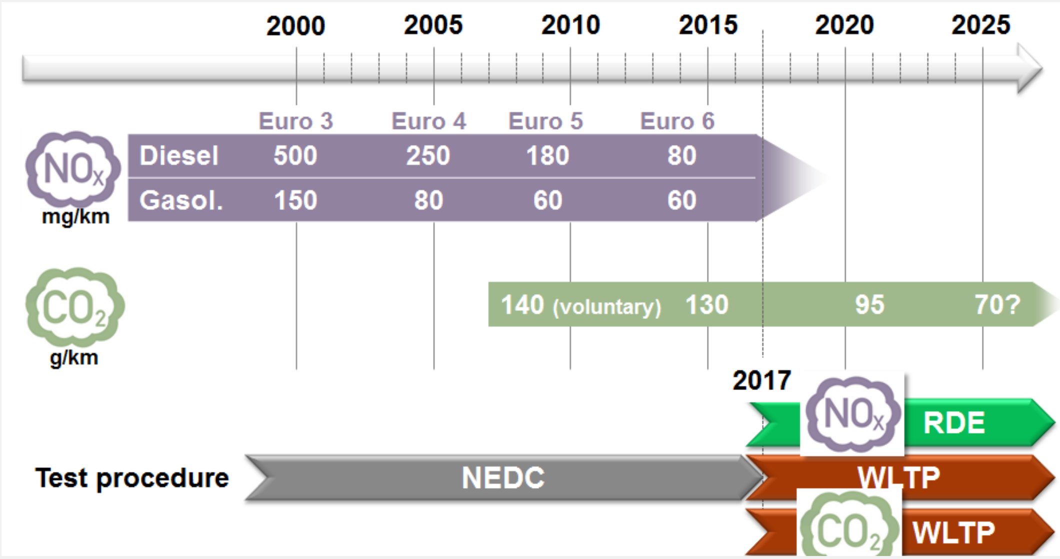
- Diesel passenger cars still account for more than 50% of the market in W. Europe, and Europe is expected to remain the biggest Diesel manufacturer in the world for the next decade.

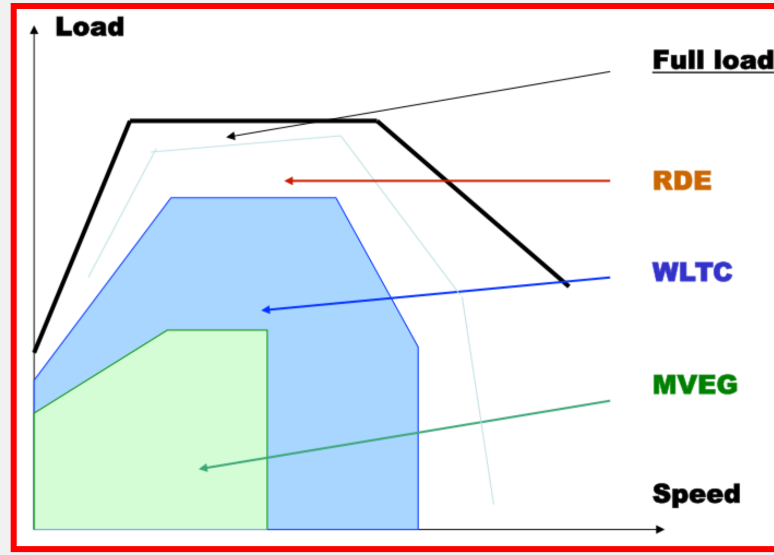




Source: ACEA

Introduction: Diesel Passenger Cars Emissions Limits



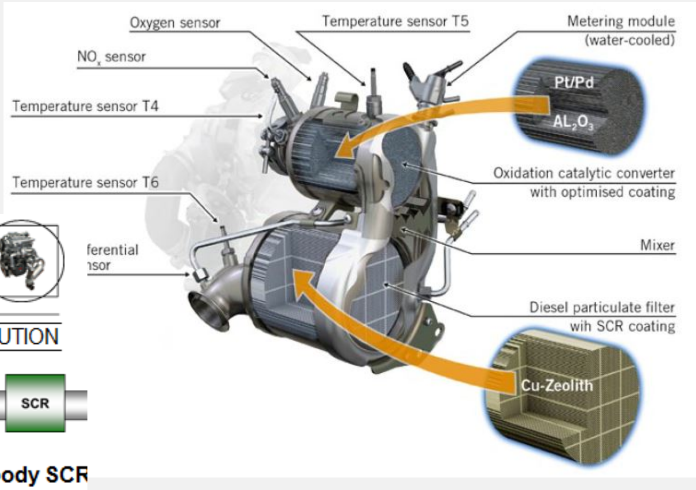


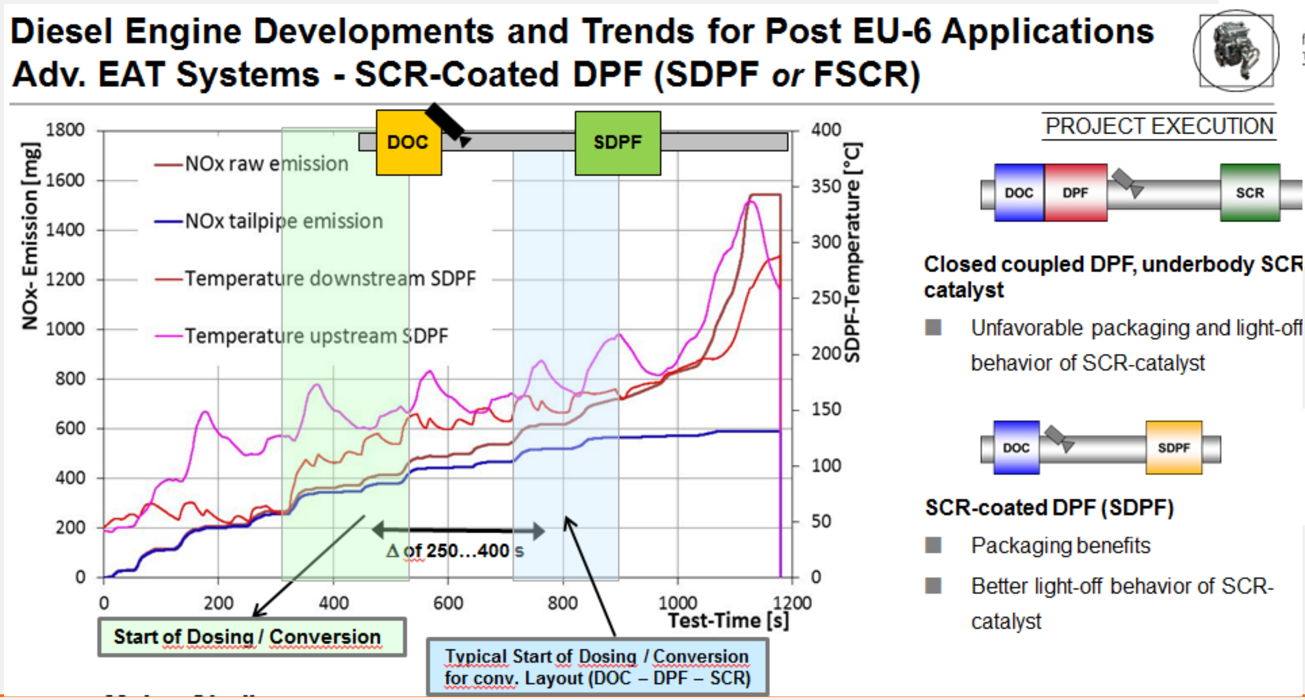
- Although still far from the «fuel neutral» US approach, EU legislation limits for NOx emissions are becoming more and more severe, but, most important, type approval procedures are going to radically change with the introduction of WLTP and real driving emission (RDE) tests.

- New test cycles expand the emission relevant area to higher loads and speeds. RDE compliance is the dominating challenge.

Introduction: Diesel Passenger Cars Emission Control

- Advanced emission control systems including in-cylinder control techniques and aftertreatment complex technologies are necessary to comply with new legislation limits.
- In this context, technologies like SCRoF (SCR on Filter), i.e. DPF with SCR coating, as well as the combination of LNT + SCRf, are becoming more and more attractive for OEMs.

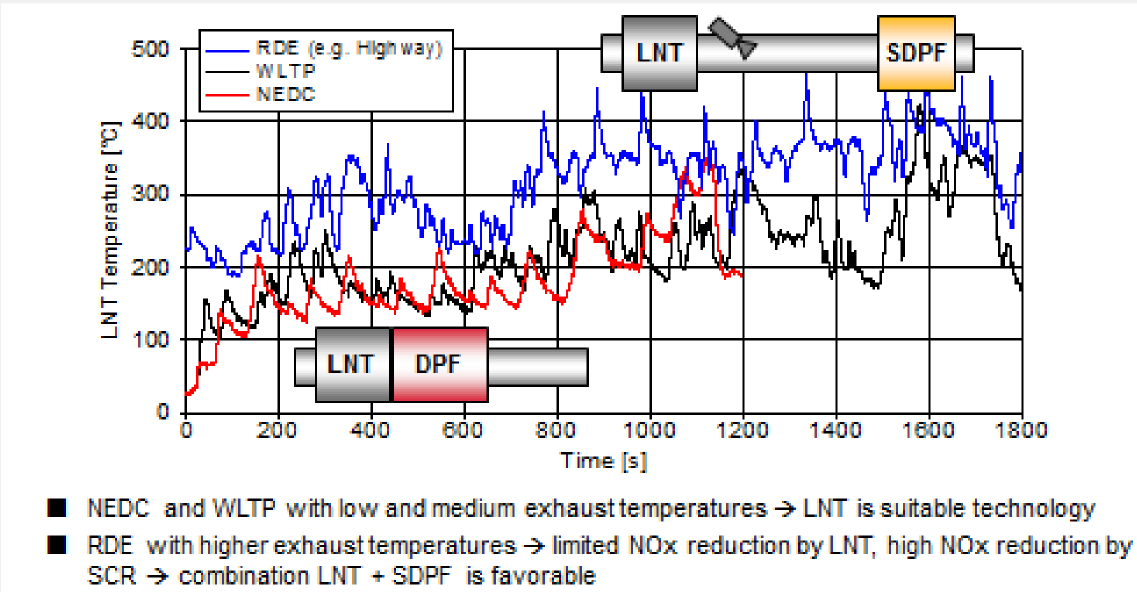




Source: Koerfer, T. et al. «Automotive Diesels facing the challenge of future emissions standards», SAE-ATA Convergence Conference, 2012, Turin, Italy

Introduction: Diesel Passenger Cars Emission Control

- Using SCR-F downstream of an LNT provides the advantage of higher NO_x conversion, especially at lower temperatures, in addition to limiting NH_3 slip from LNT which is consumed by SCR-F.



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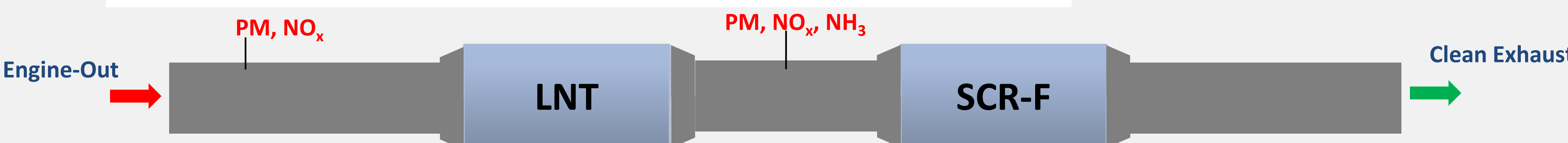


Xu, L., McCabe, R., Tennison, P., and Jen, H., "Laboratory and Vehicle Demonstration of "2nd-Generation" LNT + in-situ SCR Diesel Emission Control Systems," SAE Int. J. Engines 4(1):158-174, 2011, doi:10.4271/2011-01-0308.
Seo, C., Kim, H., and Choi, B., "De-NOx Characteristics of a Combined System of LNT and SCR according to Space Velocity," SAE Technical Paper 2011-01-2088, 2011, doi:10.4271/2011-01-2088.

Introduction: Need for Aftertreatment Modelling

As the efficiency of these advanced aftertreatment increase, their operation and control are typically becoming the bottleneck for further performance improvement.

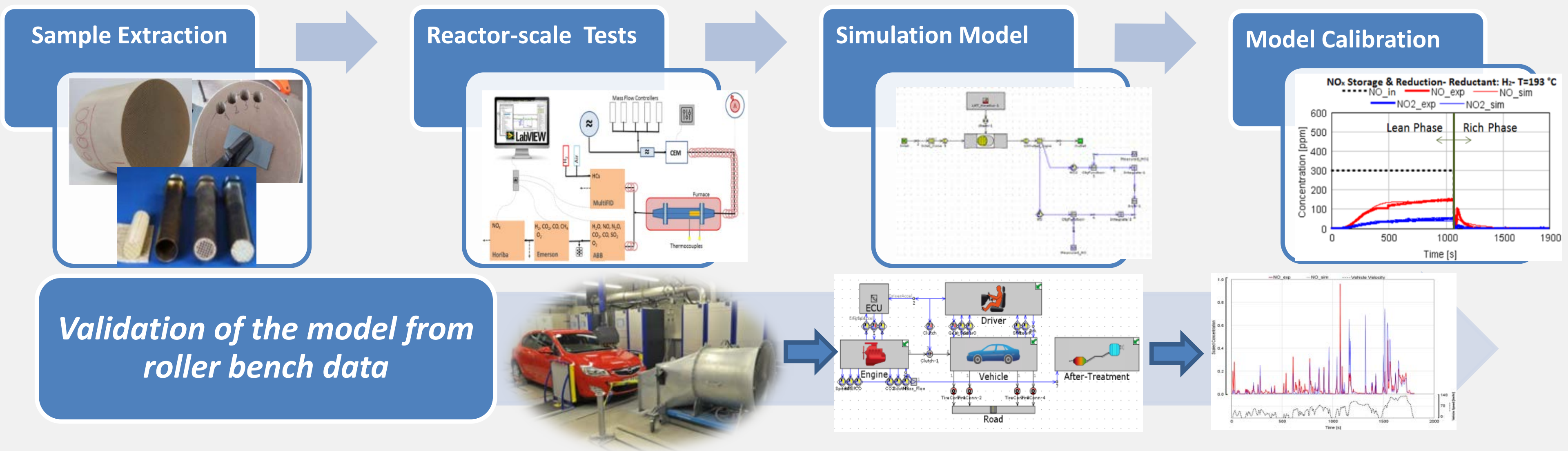
Thus, ATS control (including urea dosing, ammonia slip control, etc.) is attracting more and more attention, and model-based control is an emerging approach.

Different approaches for ATS modelling can be found in literature, which can be grouped into the following 3 categories:

1. Detailed physics-based models describing the convection-diffusion-reaction system and incorporating detailed kinetic models;
2. Map-based method or linearized black-box models;
3. Grey-box models with a reduced 1-D or 0-D approach and simplified kinetics, aiming to achieve balance between the accuracy provided by detailed models and the computational efficiency provided by black-box models.

Introduction: Need for Aftertreatment Modelling

- In order to develop suitable aftertreatment models capable of reliable predicting performance and emissions of innovative diesel powertrain systems, following steps should be taken into account:
    - Definition and performance of suitable **Synthetic Gas Bench (SGB) test protocols**
    - Development and **calibration of kinetic mechanism** based on SGB data using **simulation tools**
    - **Validation** of the model based on full scale component data using engine-out emissions over driving cycles to assess the capability of the technology to reach the future challenging emissions and fuel economy targets for diesel powertrains for passenger car applications



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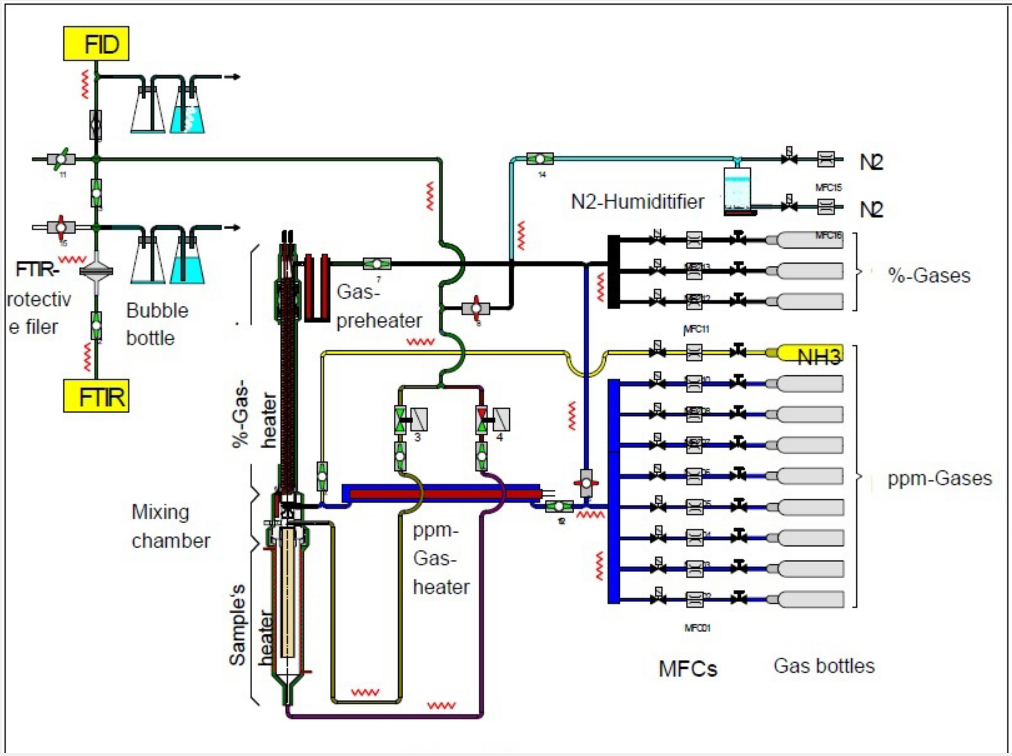
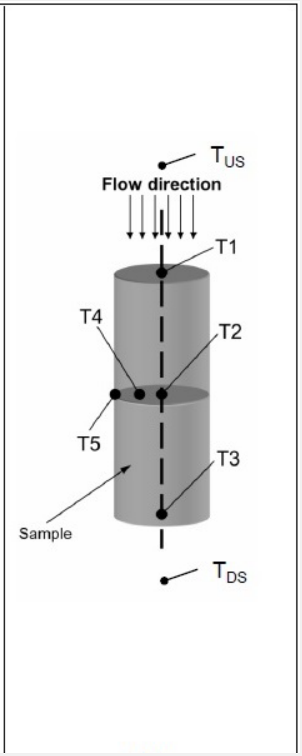
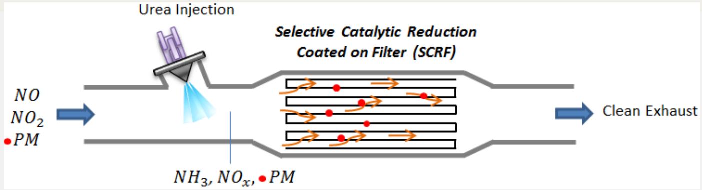
SCR on Filter: SGB Test Protocols

- SGB test protocols are defined with the aim to decouple the effects of different mechanisms, by feeding the catalyst sample with controlled species concentrations and flow rates and temperatures, thus facilitating the model calibration process.
- Tests are typically being repeated at different space velocities, and, for SCRoF, at different soot loading levels (e.g. at 0 and 8 g/L soot loadings).



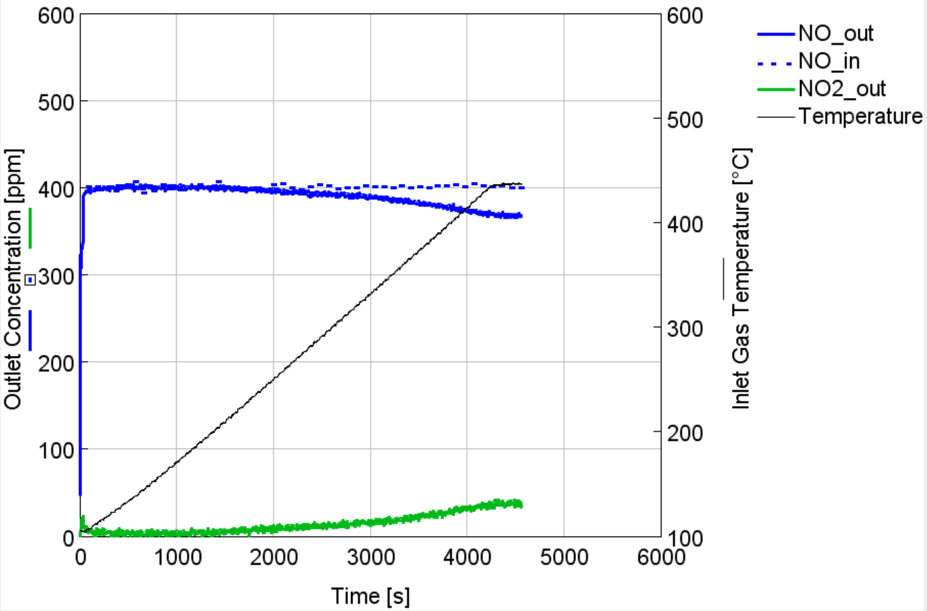


SCR on Filter: SGB Test Protocols



- NO oxidation test
- This test used to characterize the NO oxidation into NO_2, and is typically repeated for at least two different **space velocities**, such as for instance 30000 and 60000 1/hr. **Temperature is ramped up, from 100 to 430 °C** with a constant rate of 5 K/min.
- Due to absence of NH_3 in the inlet batch, NO_x reduction with ammonia mechanisms are not active.

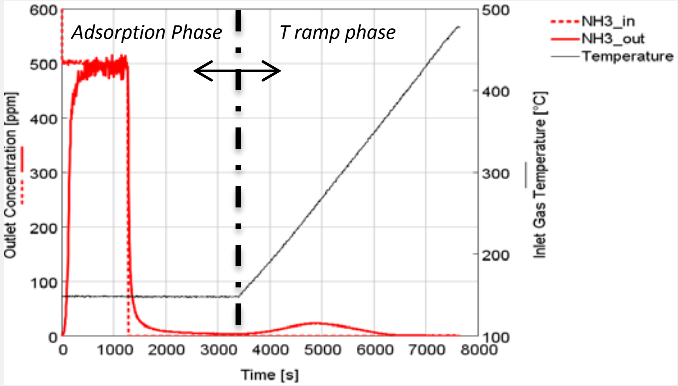
Inlet Species	Concentration
NO [ppm]	400
O_2 [%]	10
CO_2[%]	5
H_2O[%]	5
N_2	Balance



SCR on Filter: SGB Test Protocols

- Temperature Programmed Desorption (TPD) test
- TPD test is utilized to obtain ammonia storage capacity versus temperature and consists of two main parts.
- In the first phase, **NH_3 adsorption**, the inlet temperature is kept constant until the inlet NH_3 is equal to the outlet one.
- Afterwards, in the second phase (**temperature ramp)** phase, after stopping ammonia injection at the inlet, temperature is increased with a constant rate of 5 K/min.
- Test is typically repeated for different adsorption temperatures.

Inlet Species	NH_3 adsorption	T ramp
NH_3 [ppm]	500	-
H_2O[%]	10	10
N_2	Balance	Balance

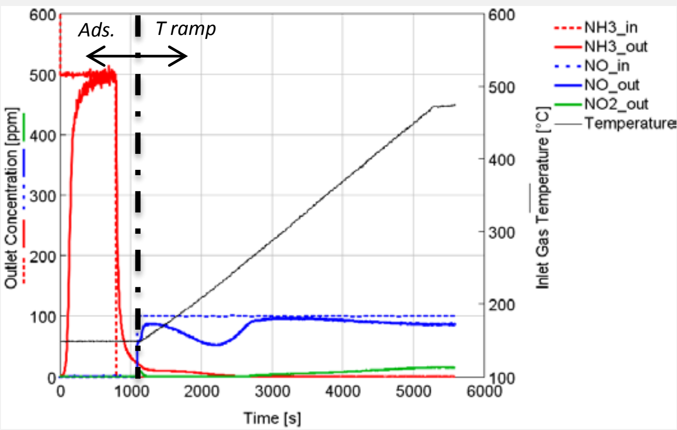


SCR on Filter: SGB Test Protocols

- Temperature Programmed Reduction (TPR) test
- Performed similarly to TPD, with the aim to characterize NH_3 oxidation, standard, slow and fast SCR reactions using different NO_2/NO_x ratios.
- Test is repeated for different inlet batches.

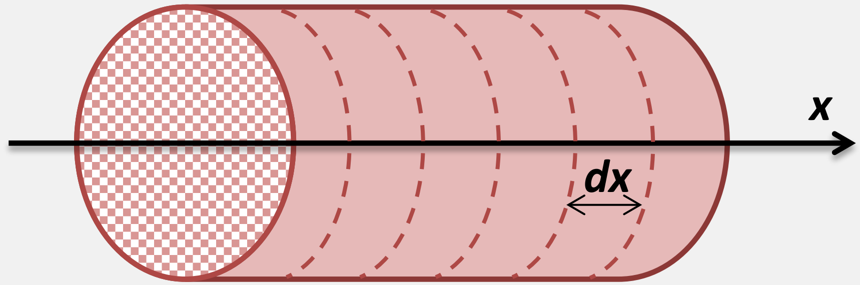
$$\begin{array}{ll} Standard\ SCR & 4NH_3 - Z + 4NO + O_2 \rightarrow 4N_2 + 6H_2O + 4Z \\ Fast\ SCR: & 2NH_3 - Z + NO + NO_2 \rightarrow 2N_2 + 3H_2O + 2Z \\ Slow\ SCR: & 4NH_3 - Z + 3NO_2 \rightarrow 3.5N_2 + 6H_2O + 4Z \end{array}$$

Inlet Species	NH_3 ads.	T ramp			
		NH_3 oxidation	Standard SCR	NO_2/NO=1	NO_2/NO=2
NH_3 [ppm]	500	-	-	-	-
NO [ppm]	-	-	100	50	33.33
NO_2 [ppm]	-	-	-	50	66.67
O_2 [%]	-	10	10	10	10
H_2O [%]	10	10	10	10	10
N_2	Balance	Balance	Balance	Balance	Balance



SCR on Filter: Simulation Model

- The 1D-CFD, GT-SUITE, model is based on the following assumptions:
- Any non-homogeneity and non-uniformity of flow field and thermal field in a defined cross-section is neglected.
- Only variations in flow field direction along the catalyst length (x) is considered, such that the catalyst brick is divided into several sub-volumes with length dx.



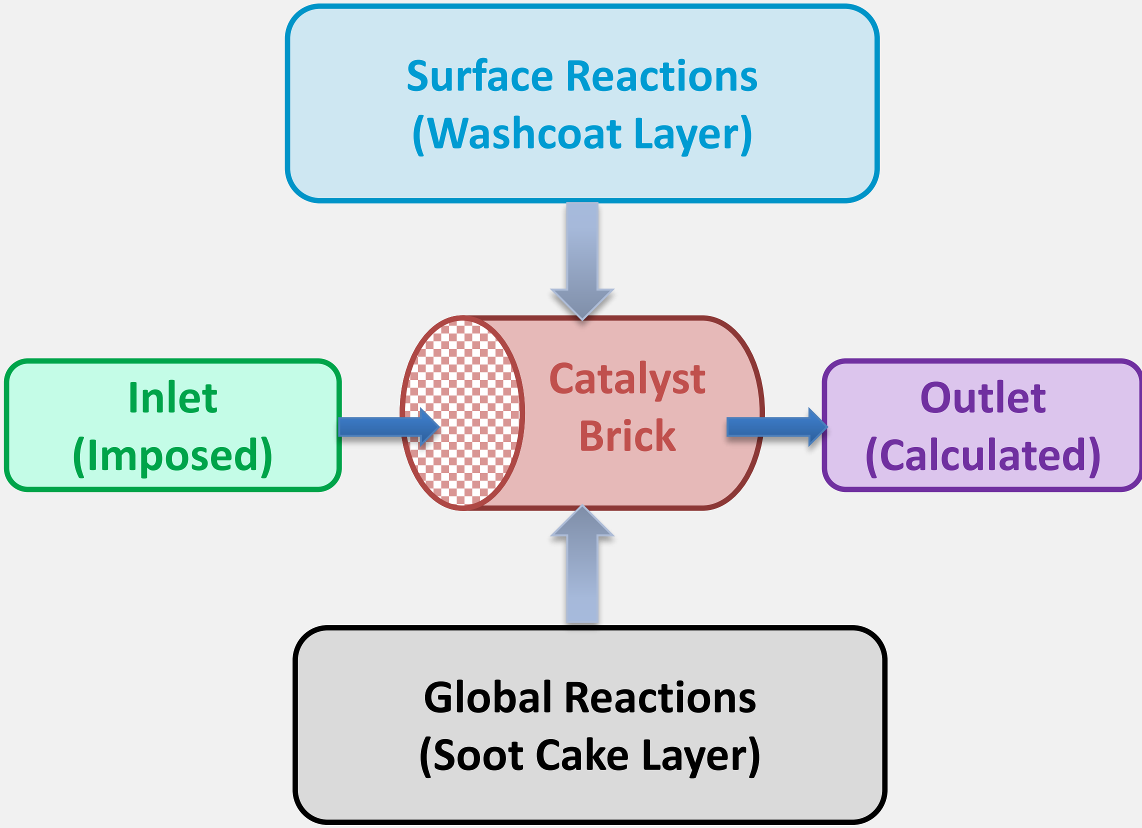
- The main governing equations include continuity, momentum, solid and gas energy balances.
- Quasi-steady approximation can be applied, since the residence time of the gas in the reactor compared to other time scales is short.
- Global kinetic mechanism is considered.

SCR on Filter: Simulation Model

- The goal is to calibrate the kinetic parameters including **site density**, **pre-exponent multiplier** and **activation energy** of each reaction. Arrhenius form function $R = A \exp\left(-\frac{E_a}{RT}\right)$ is used for the kinetic constant.

Site	SCR Reactions
Zeolite	$Z + NH3 \leftrightarrow ZNH_3$
Zeolite	$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$
Zeolite	$NO + 0.5O_2 \leftrightarrow NO_2$
Zeolite	$4ZNH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O + 4Z$
Zeolite	$2ZNH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O + 2Z$
Zeolite	$4ZNH_3 + 3NO_2 \rightarrow 3.5N_2 + 6H_2O + 4Z$
Site 2	$NO_2 + 2NH_3 + Site \leftrightarrow NH_4NO_3\text{-}Site + N_2 + H_2O$

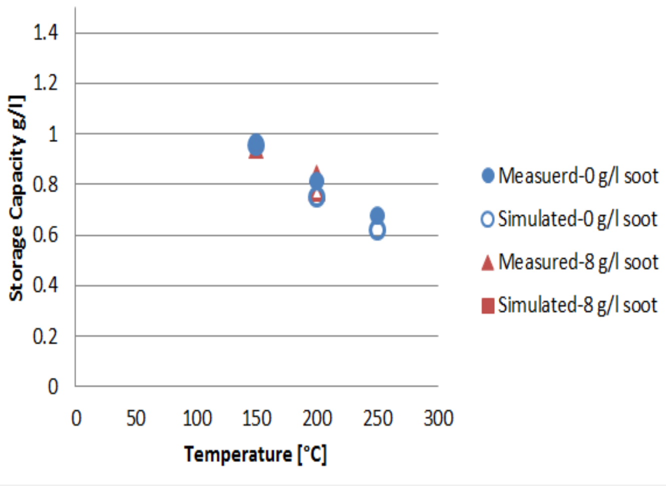
Site	Soot Conversion
Cake & Washcoat Layers	$C + NO_2 \rightarrow CO + NO$
Cake & Washcoat Layers	$C + 2NO_2 \rightarrow CO_2 + 2NO$
Cake & Washcoat Layers	$C + O_2 \rightarrow CO_2$
Cake & Washcoat Layers	$C + 0.5O_2 \rightarrow CO$

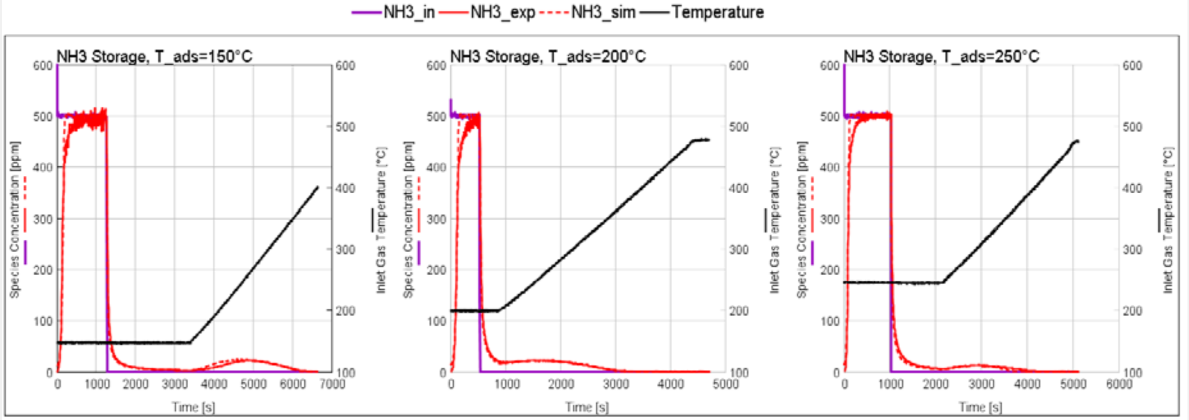


SCR on Filter: Results

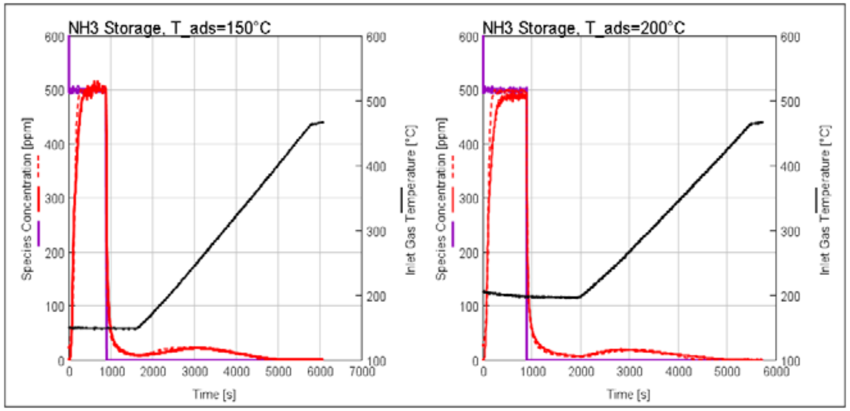
TPD test results

- **Soot has minor impact on NH_3 storage capacity** and slightly improves the storage capacity, specifically at T<250 °C, due to its higher geometric surface area.
- **NH_3 storage capacity decreases by increasing temperature**, almost linearly.





(a) Soot free sample



(b) Soot loaded sample 8 g/l

SCR on Filter: Results

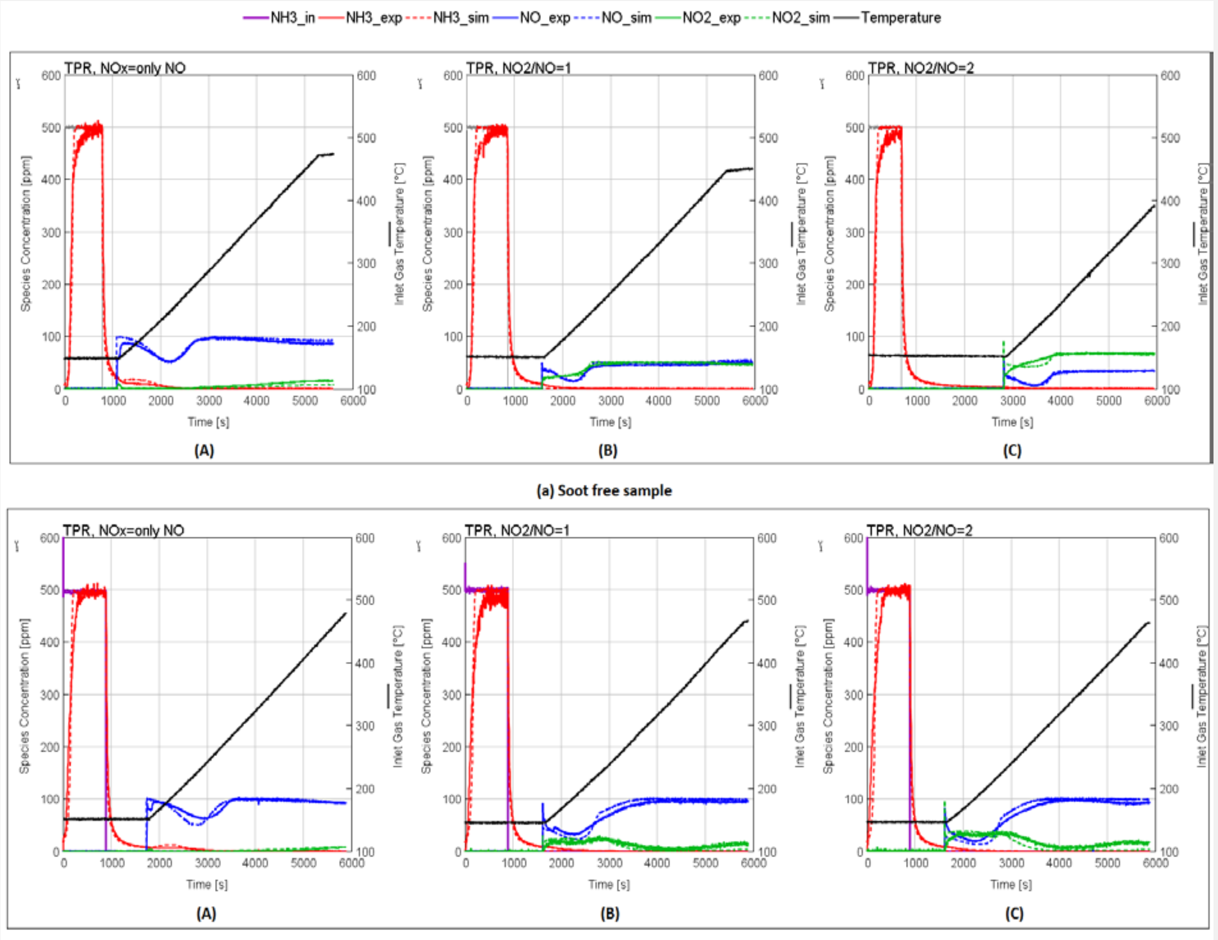
- **TPR test results**

- NO_x conversion is function of temperature, NO_2/NO_x ratio and availability of the reductant.

- At lower T, initially NO_2 concentrations drop and can be related to formation of NH_4NO_3 → higher conversion of NO_2 with respect to NO at lower T.

- Soot conversion varies the local NO_2/NO_x ratio → alters the SCR reaction pathway.

- Maximum conversion is observed at equimolar local NO_2/NO.



(a) Soot free sample

(b) Soot loaded sample 8 g/l

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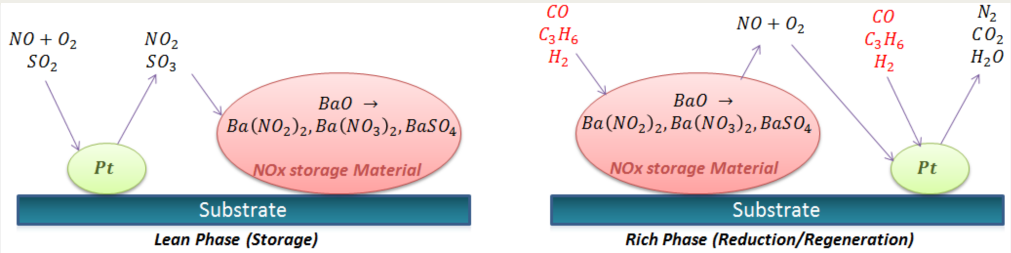
Lean NO_x Traps: SGB Test Protocols

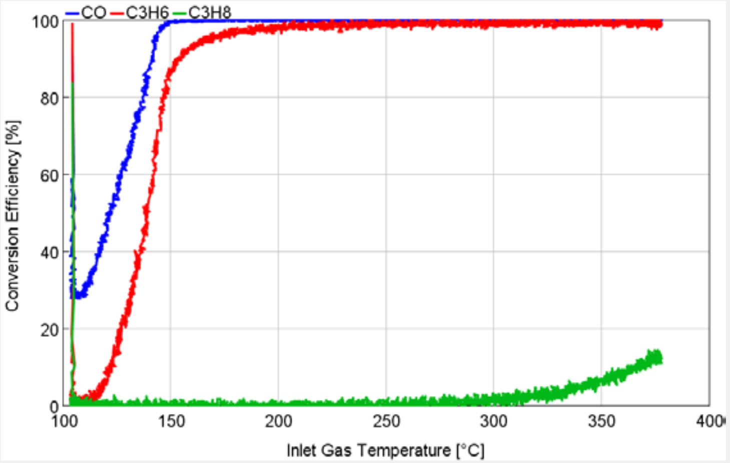


LNT reactor-scale experiments:

- Light-off test

It characterizes CO, C_3H_6 (fast oxidizing HCs) and C_3H_8 (slow oxidizing HCs) oxidation mechanisms during a **temperature ramp, from 100 to 370 °C at constant standard space velocity**. Due to absence of NO_x in the inlet batch, NO_x storage and reduction mechanisms are not active.

Inlet Species	Concentration
HC [ppm]	400
CO [ppm]	300
H_2 [ppm]	60
O_2 [%]	10
CO_2[%]	5
H_2O[%]	5
N_2	Balance



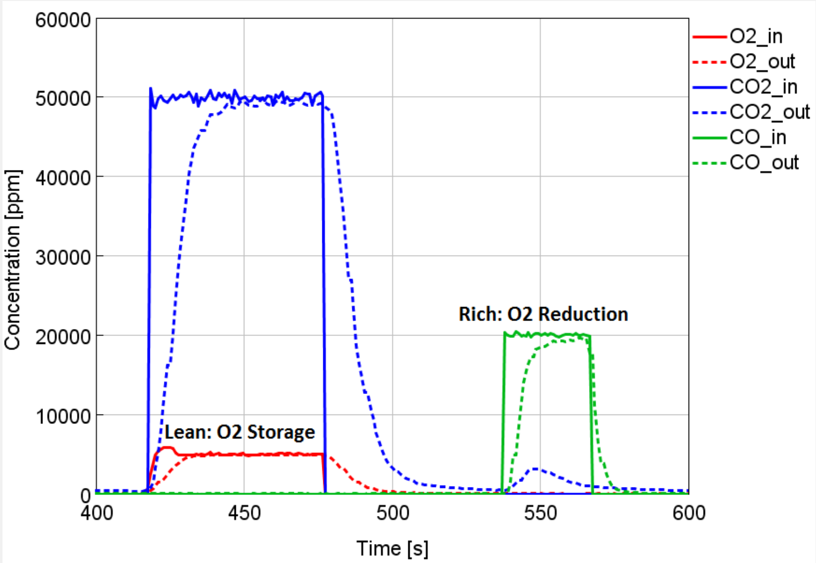
Lean NO_x Traps: SGB Test Protocols

- Oxygen Storage Capacity (OSC) test

It consists of lean phase, in which oxygen is stored on ceria sites, followed by a rich phase in which CO and H_2 clean-off the stored oxygen from ceria. The test is repeated at **different temperature levels, ranging from 150 to 450 °C at constant standard space velocity**.

Due to absence of NO_x in the inlet batch, NO_x storage and reduction mechanisms are not active.

Inlet Species	Lean	Rich
CO [%]	-	2
O_2 [%]	0.5	-
CO_2[%]	5	-
H_2O[%]	5	5
N_2	Balance	Balance

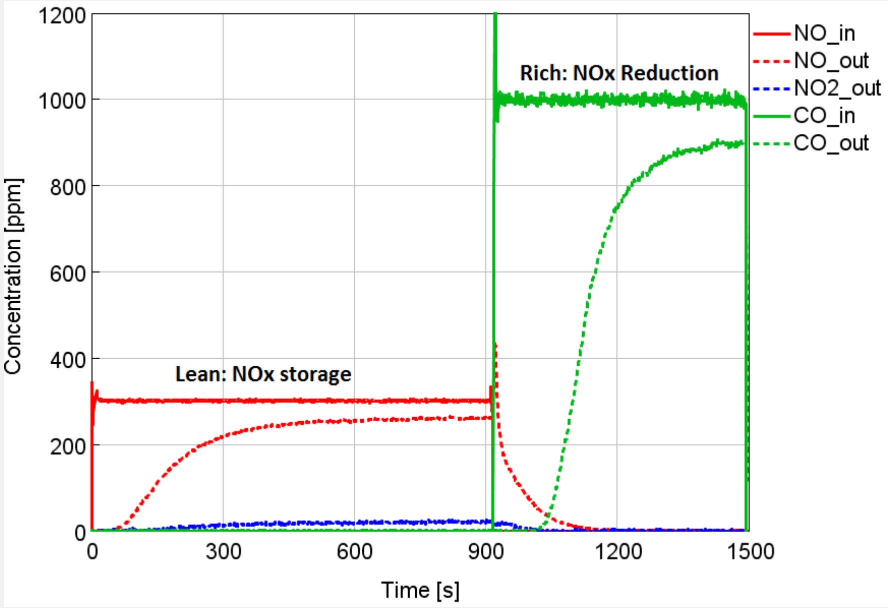


Lean NO_x Traps: SGB Test Protocols

- NO_x Storage and Reduction (NSR) test

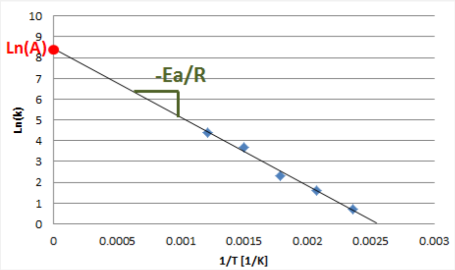
It consists of lean phase, in which NO_x is stored on barium sites, followed by a rich phase in which CO, H_2 and C_3H_6 reduce the stored NO_x. The test is at **different temperature levels, ranging from 150 to 450 °C at constant standard space velocity**.

Inlet Species	Lean	Rich
NO [ppm]	300	-
Reductant [ppm]	-	CO (1000), H_2 (1000), C_3H_6 (100)
O_2 [%]	0.5	-
CO_2[%]	5	-
H_2O[%]	5	5
N_2	Balance	Balance



Lean NO_x Traps: Global Kinetic Mechanism

- By means the SGB test protocols, the global kinetic mechanism can be calibrated for the following reactions.



Site	NOx Storage and Reduction (NSR)
PGM	$NO + 0.5O_2 \leftrightarrow NO_2$
Ba	$BaO + 2NO + 1.5O_2 \leftrightarrow Ba(NO_3)_2$
Ba	$BaO + 2NO + 0.5O_2 \leftrightarrow Ba(NO_2)_2$
Ba	$BaO + 3NO_2 \leftrightarrow Ba(NO_3)_2 + NO$
Ba	$Ba(NO_3)_2 + 8H_2 \rightarrow BaO + 2NH_3 + 5H_2O$
Ba	$Ba(NO_3)_2 + 10/3NH_3 \rightarrow BaO + 8/3N_2 + 5H_2O$
Ba	$Ba(NO_3)_2 + 2NH_3 \rightarrow BaO + 2N_2O + 3H_2O$
...	Other reactions of NOx reduction with CO and HC and H_2over the PGM and barium sites

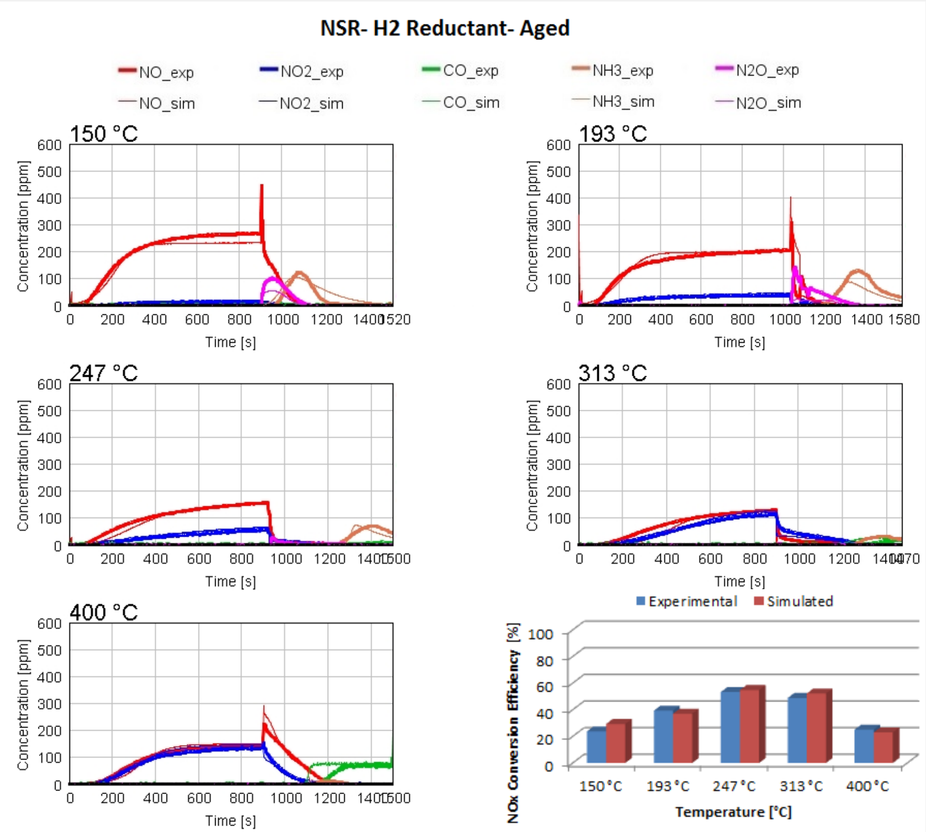
Site	Light-off
PGM	$C_3H_6 + 3H_2O \rightarrow 6H_2 + 3CO$
PGM	$C_3H_8 + 3H_2O \rightarrow 7H_2O + 3CO_2$
PGM	$CO + 0.5O_2 \rightarrow CO_2$
PGM	$H_2 + 0.5O_2 \rightarrow H_2O$
PGM	$C_3H_6 + 4.5O_2 \rightarrow 3CO_2 + 3H_2O$
PGM	$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$

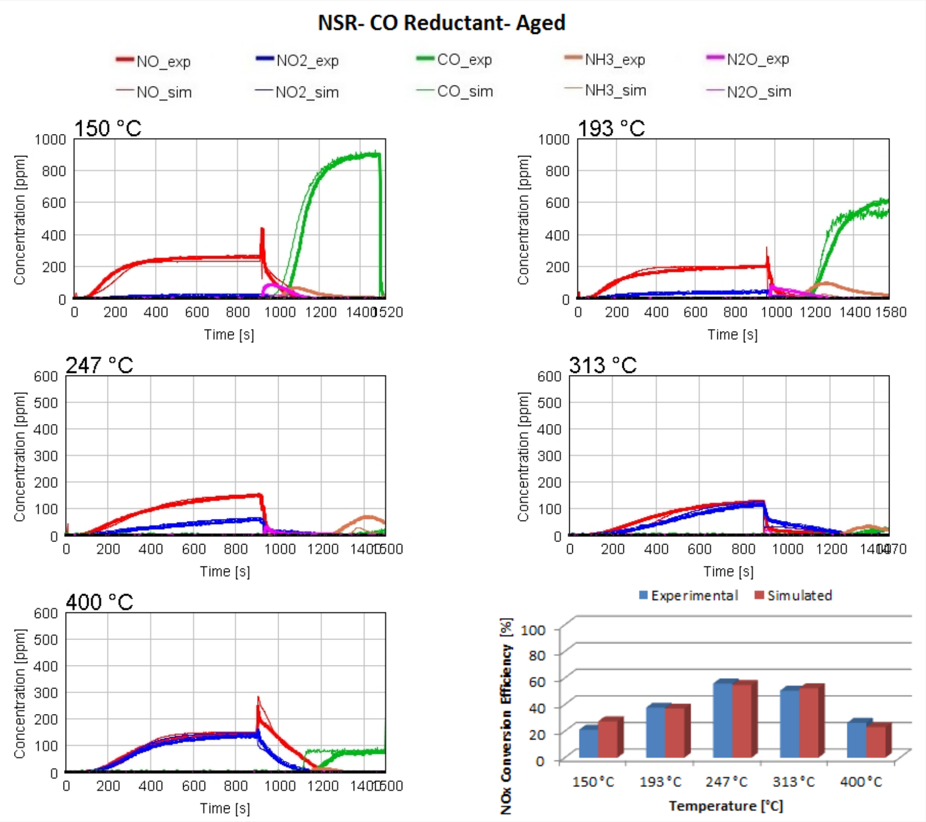
Site	Oxygen Storage Capacity (OSC)
Ce	$Ce_2O_3 + 0.5O_2 \rightarrow 2CeO_2$
Ce	$2CeO_2 + CO \rightarrow Ce_2O_3 + CO_2$
Ce	$2CeO_2 + H_2 \rightarrow Ce_2O_3 + H_2O$
Ce	$2CeO_2 + 1/9C_3H_6 \rightarrow Ce_2O_3 + 1/3\,H_2O + 1/3CO_2$
PGM	$CO + H_2O \leftrightarrow CO_2 + H_2$

- Kinetic parameters including **site densities**, **pre-exponent multiplier** and **activation energy** of each reaction are calibrated by matching the simulation results of catalyst outlet concentrations for NO, NO_2, H_2, CO, HC, NH_3 and N_2O species with measured values from SGB experiments.

Lean NO_x Traps: Results

- Predicted NO_x storage and reduction results follow the measured data with satisfactory agreement. As expected, the maximum conversion efficiency is observed at medium temperatures.





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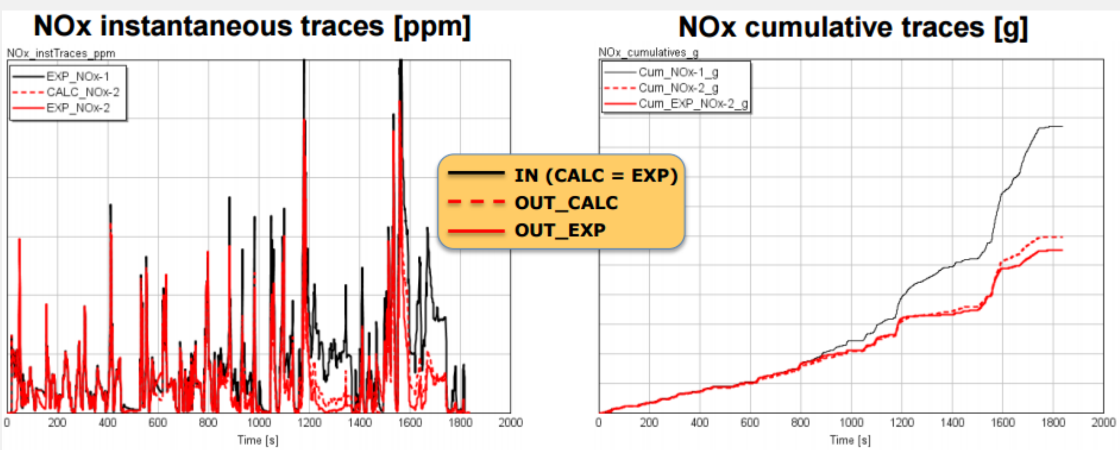
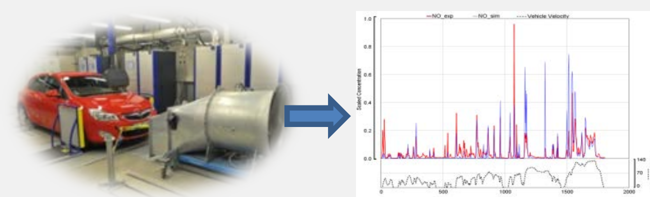
Conclusions

- Tighter emission regulations, specifically in terms of NO_x, invoke the necessity of implementing advanced aftertreatment technologies, such as SCR-F and LNT + SCR-F.
- Numerical models of aftertreatment devices for NO_x emissions control can be built and calibrated by means of suitable SGB tests, which allow to decouple the effects of different mechanisms.
- Afterwards, reactor scale calibrated models can be up-scaled to model full-size components in order to asses the capability of the aftertreatment system to reduce NOx emissions under different driving cycles.

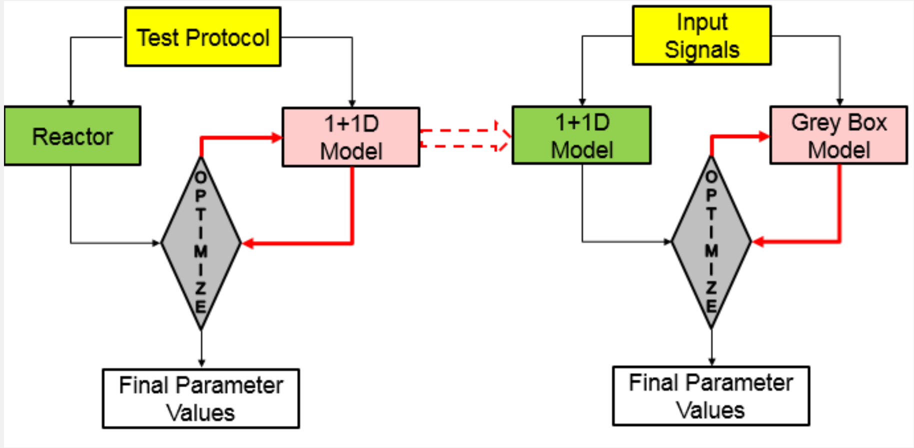


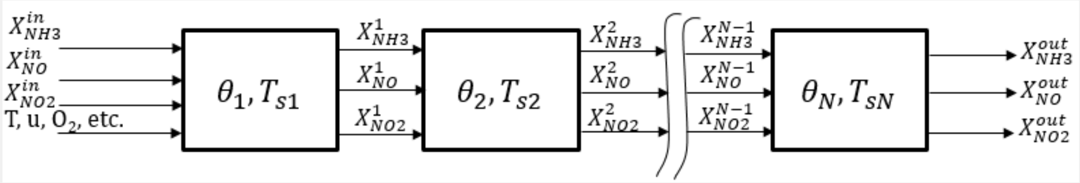


P. Ferreri, M. Rimondi, Development of a SCR on Filter GT-SUITE 1-D Global Kinetic Model: From Reactor-Scale to Full Transient Engine-Scale Evidence, GT User Conference, Frankfurt, Germany (2015)

Conclusions

- Finally, aftertreatment model can be further simplified to reduced order models to be implemented in Real Time applications such as Engine Control Units (ECU) and Hardware in Loop (HiL) systems, thanks to their lower computational time, thus paving the way for a wider diffusion of model based aftertreatment systems control.





Santhosh R. Gundlapally, Iakovos Papadimitriou, and Syed Wahiduzzaman
Development of ECU Capable Grey-Box Models from Detailed Models - Application to a SCR Reactor,
Emission Control Science and Technology, Volume 2, Issue 3, 2016

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